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Near Infrared Measurement of Cotton Fiber Micronaire by Portable Near Infrared Instrumentation

Abstract In the U.S.A., cotton is classed (primary quality parameters) by the Uster® High Volume Instrument (HVI), which must be maintained under tightly controlled laboratory environmental conditions. Improved and fast response quality measurement systems and tools are needed to rapidly assess the quality of cotton. One key area of emphasis and need is the development and implementation of new fast-response quality measurements that can be used not only in the laboratory but which also can be adapted to field and at-line quality measurements. A program was implemented to determine the ability of portable near-infrared (NIR) instrumentation to monitor critical fiber properties of cotton samples in the laboratory, at-line, and in the field, with initial emphasis on the laboratory measurement of cotton fiber micronaire. Micronaire is a key cotton property, and it is an indicator of the fiber's maturity and fineness. Distinct NIR spectral differences between samples with varying micronaire were observed. A comparative evaluation was performed to determine optimum instrumental conditions for laboratory cotton micronaire measurements. The comparative evaluation established that the optimum instrumental conditions for laboratory measurements of micronaire was obtained with the use of a glass-covered sampling port and increased instrumental gain, with high R^2 values, low residuals, and with $\leq 12\%$ outliers. For a NIR measurement with potential for multiple simultaneous analyses and non-laboratory measurements, the micronaire measurement was fast (< 3 min per sample) and easy to perform. The rapid and accurate laboratory measurement of cotton fiber micronaire with portable NIR instrumentation was demonstrated.

Key words near infrared, cotton, micronaire, portable instrument

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Historically, cotton has been graded or classed for quality by a person ("classer") evaluating cotton samples by hand. However, over the last few decades, great strides have been made in the instrument classing of cotton, which serves to remove the subjectivity and classer-to-classer variabilities of human classers. High-volume instruments have been commercialized for cotton quality classing, and these techniques are widely used in developed and heavy cotton producing countries around the world. The Agricultural Marketing Service (AMS) of the United States Department of Agriculture (USDA) uses a high-volume instrument to classify U.S. cotton fiber [1]. At present, the high-volume instrument used by the AMS is the Uster® High Volume Instrument (HVI). The main quality attributes and properties used to classify cotton are length, length uniformity, strength, color, trash, and micronaire. The present version of HVI uses an air resistance method to measure fiber micronaire. The HVI is very fast (~30 s to classify a cotton sample for the six quality parameters), but it and all other high-volume classing machines are laboratory instruments, expensive, and require that measurements be performed in a tightly controlled conditioned laboratory.

U.S. cotton competes in a global market, and most of the cotton produced in the U.S.A. is exported, primarily to China. With the continued demand for improved quality assessment of cotton fiber prior to use, there is a growing need for the continual improvement of cotton quality measurements and for the development of rapid and precise quality measurements that can be utilized by the global marketplace. Ideally, these improved cotton quality measurements could be performed both in the laboratory and outside of the laboratory (at-line, on-line, and/or field analyses). On-line quality and process measurements are those that can be performed during processing on the manufacturing line (e.g., ginning); at-line measurements are those performed in the manufacturing area but not on the production equipment; field measurements can be considered as "breeder" or producer analyses, and are those measurements performed directly on the cotton itself in the cotton field. These non-laboratory or remote quality assessments have the potential to result in the vertical integration of the cotton quality chain from the cotton field to final fabric.

The joint need for rapid and precise laboratory and non-laboratory instrumental measurements make the use of portable, hand-held instruments very attractive. A previous comparative evaluation verified the "universal" nature of near-infrared (NIR) measurements of micronaire and its components, using commercial bench-top and portable NIR units [2]. Micronaire is a measure of the cotton fiber's resistance to air flow per unit mass, and it is a function of the fiber's maturity and fineness [1,3–5]. In a recent study, a small, common sample set of cotton fiber samples was analyzed on four bench-top and two portable NIR analyzers from four vendors [2]. Good spectral agreement was observed between the bench-top and portable NIR analyzers for the cotton fibers, and the rapid laboratory measurement of cotton fiber micronaire by multiple commercial bench-top and portable NIR analyzers was shown to be feasible. However, additional research and operational/instrumental optimization is required to fully establish the feasibility and capabilities of portable NIR instrumentation to perform rapid, precise, and accurate laboratory measurements of cotton fiber micronaire. Further, the establishment of the feasibility of laboratory measurements of cotton fiber micronaire would be used to gain valuable insight into the potential for at-line and field NIR measurements of fiber micronaire. The objective of this paper is to determine the feasibility and capabilities of portable NIR instrumentation to perform rapid and accurate laboratory measurements of cotton fiber micronaire.

Near Infrared Spectroscopy

Fundamentals

The use of NIR spectroscopy and applications for agriculture, fiber, and textile products are many (to include cotton fiber micronaire), and the use of NIR spectroscopy in these areas continues to grow [6–15]. The use of portable, scanning NIR instrumentation for both laboratory and non-laboratory analyses is a major growth area for NIR spectroscopy, and there is much interest in applications for cotton fibers. NIR measurements and instrumentation offer several advantages that make the use of this technique very attractive for both laboratory and non-laboratory applications, to include analyses that are often fast, accurate, precise, easy to perform, non-destructive, require minimal sample preparation, and have capabilities for analyses of multiple properties that can be qualitative and/or quantitative in nature. NIR instrumentation is often rugged, easy to use and maintain, requires minimal operator training for routine operation, and has network capabilities. The NIR measurement must be calibrated to a reference method, so it is a secondary rather than a primary analytical measurement. In order to calibrate the NIR instrument and its complex spectra to a reference method, chemometric mathematical modeling is often used, such as Multiple Linear Regression (MLR), Partial Least Squares (PLS), Principal Component Analysis (PCA), and Principal Component Regression (PCR). These chemometric techniques often require the use of a large number of well-defined samples.

The NIR spectral region is located between the visible and infrared spectral regions, and it is normally referred to as the spectral region from 1100–2500 nm (~9000–4000 cm^{-1}) [16–19]. In this region, the NIR absorbances are most often due to overtone and combination bands of the fundamental absorbances observed in the infrared spectral regions.

The chemical species most often observed in the NIR spectral region are CH_n, NH_n, and OH, but moderate to strong absorbances can also be detected for carbonyl (CO), sulfydryl (SH), and amide ($CONH_n$) chemical groups. Since the presence of overtone and combination bands can lead to broad NIR spectral absorbances, a typical NIR absorbance spectrum can look similar to a visible absorbance spectrum; hence the need to often use chemometric mathematical modeling for calibration of the NIR technique to a reference method. In solids (such as cotton fiber), the light from the instrument's source is reflected diffusely from the sample's surface. This diffuse reflectance, R, is collected at varying wavelengths (λ) by the instrument over the wavelength range of interest, and the diffuse reflectance can be converted to absorbance by the relationship:

$$A_{\lambda i} = -\log R_{\lambda i} = \log (1/R_{\lambda i}) \qquad (1)$$

The NIR absorbance spectrum is obtained by plotting A versus λ over the wavelength interval of interest, and often the absorbance spectra are complex. As mentioned previously, the complex spectra often necessitate the use of chemometric mathematical modeling to calibrate the instrument to the reference method.

Critical Elements

The present HVI does not use NIR, but earlier HVIs did use a filter-based NIR (NIR HVI) to measure maturity. In 1991, NIR HVIs to measure maturity were put on display at the International Textile Machinery Association exhibition in Hanover, Germany. Two U.S. companies, Motion Control and Spinlab, introduced the instruments for application in textile mills and to grade raw cotton. The instrumentation was marketed worldwide for several years before it was discontinued based on independent evaluations in 1994 that gave unacceptable results [7]. Five critical elements were identified as causal factors in optimizing NIR HVI performance to measure cotton fineness and maturity [7], and they also apply equally well to micronaire measurements by NIR. This is because micronaire is a function of fineness and maturity. These critical elements were:

- the reference method (regardless of type or instrument) must be drift-free and its variability reduced to an acceptable level;
- before accepting or rejecting reference method data evaluated by the R^2_{MAXREG} test statistic (defined below), the tolerance in the R^2_{MAXREG} test statistic value should be specified;
- if feasible, specifications must be established for both the minimum surface area of cotton sample to scan and the minimum pressure to press the fibers against the quartz window;

- to optimize the NIR calibration equations for raw (heterogeneous) cottons, the same specimen from each sample must be analyzed first by NIR and then by the reference method, or the cotton must be homogenized prior to analysis;
- perimeter and wall thickness are the fundamental measures and should be used to understand NIR prediction errors.

Coefficients of determination (R^2) between a sample property (Y) and NIR spectra (X) are limited by the accuracy of the reference method data means of each sample in the data set. Reference method data diagnostics have been restricted to the standard deviation of the means of each sample and the pooled standard deviation of the data. The test statistic, R^2_{MAXREG}, sets the upper limit on R^2, assuming an ideal regression model and no errors in the X values. The available replicate Y values on each sample are split into halves, the means computed for each half, and the corresponding means correlated to produce a measure of split sample correlation, M_{SPLIT}. Here M_{SPLIT} is a measure of the fit of the paired means to the line $Y = X$ and is used to compute R^2_{MAXREG} for means based on all the replicate Y values on each sample. Note that R^2_{MAXREG} is sensitive to both random error and systematic components of variation in the reference method data. In effect, R^2_{MAXREG} is the maximum possible R^2 between the reference data sample means and the independent variable (NIR spectra). The goal in the published work, concerned with optimizing NIR HVI performance, was tight tolerances in performance results. The permissible deviation from the specifications was held to a minimum. Examples of specifications with tight tolerances were: R^2_{MAXREG} value ≥ 0.95, fast analysis (5 s per sample), and R^2 prediction results between a fiber property and NIR ≥ 0.95.

In this paper, we begin the task of identifying the causal factors in NIR performance in measuring micronaire by portable instrumentation by means of a comparative evaluation to determine the basic feasibility and capabilities of portable NIR instrumentation for laboratory micronaire measurements, with the aim to develop portable NIR methods with acceptable "end-state criteria" – agreed to by cotton industry representatives. These tolerances are not as tight as in the published work related to NIR HVI. Thus, evaluation of R^2_{MAXREG}, optimization of all applicable critical elements to improve portable NIR performance, and correlations of uncorrected spectra do not necessarily apply to end-state criteria that have been successfully met or exceeded in the present paper.

Table 1 HVI reference micronaire descriptive statistics.

PARAMETER	GROUP 1	GROUP 2	GROUP 3	TOTAL
Number of Samples (*n*)	104	69	18	*191*
Mean	4.22	4.24	4.17	*4.22*
Range	3.05	2.67	2.93	*3.13*
Minimum	2.60	2.89	2.52	*2.52*
Maximum	5.65	5.56	5.45	*5.65*
Std Dev (Range)	0.56	0.59	0.77	*0.59*

Figure 1 Laboratory cotton fiber measurements with the portable NIR analyzer.

Experimental Details

Cotton Samples

For the laboratory evaluations, 191 selected ginned cotton fiber samples, with a wide range of micronaire values and representing over 100 cotton varieties, were used (micronaire range from 2.52 to 5.65 micronaire units). The 191 samples were collected from three well-defined sets of samples and incorporated a wide range of cotton varieties. The HVI-1000 unit at the Southern Regional Research Center (SRRC-ARS-USDA, New Orleans, LA, U.S.A.) was used to determine the micronaire reference values for all cotton samples, and there were five micronaire measurements per cotton sample. For all laboratory measurements, the cotton samples were conditioned for a minimum of 24 h at 70 ± 2°F and 65 ± 2% relative humidity (RH). Descriptive statistics for the HVI micronaire measurements are given in Table 1. Five measurements were taken for each sample with the portable NIR analyzer, with a different portion of the sample measured each time. The NIR measuring head is placed directly on the fiber sample (5.0 ± 0.5 g) to obtain the NIR measurement of the sample. The 5 g sample mass was randomly drawn from the large laboratory sample remaining after HVI tests. This mass of cotton yielded an acceptable sample presentation and represented reflection at infinite thickness (no "thin spots" or stray light effects) for the portable NIR. Averaged micronaire and spectra were computed and used to construct the NIR algorithms.

Portable NIR Analyzer

The Brimrose Luminar 5030 mini-spectrometer is a portable, hand held NIR analyzer that was used in this evaluation (Figure 1). An acousto-optic tunable filter (AOTF) is used to measure the sample's diffuse reflectance from 1100–2300 nm in 2 nm increments [20]. The principle of the AOTF is based upon the acoustic diffraction of light in an anisotropic medium. The device consists of a piezo-electric transducer bonded to a birefringent crystal. When the transducer is excited by an applied RF signal, acoustic waves are generated in the crystal. The propagating acoustic wave produces a periodic modulation of the refractive index. This provides a moving phase grating that under proper conditions will diffract portions of an incident light beam. For a fixed acoustic frequency, a narrow band of optical frequencies satisfies the phase matching conditions and is cumulatively diffracted. As the RF frequency is changed, the center of the optical band-pass is changed accordingly so that the phase matching condition is maintained.

There are two 5 mm sampling ports, or "measuring heads" – an open port and a sapphire glass port (in which a thin sapphire glass is placed on the port). The use of sapphire glass permits improved sampling consistency for the fiber samples, as the fibers are pressed as a uniform surface against the sampling port when the portable NIR analyzer is placed directly on the fiber sample. In this evaluation, each sample was measured with an open port (without glass, NG) and with the sapphire glass port (with glass, G) at both instrument gain = 1 (300 scans per sample) and instrument gain = 2 (400 scans per sample) – a total of four instrument/operational settings and conditions per sample.

For normal operations (data collection, data manipulation, etc.), a computer is used to operate the NIR analyzer, using the Brimrose SNAP software [21]. Chemometric statistical modeling and calibrations were performed with the Camo® Unscrambler chemometric software package [22].

End-State Criteria

"End-state criteria" are the key stated goals for an analytical measurement. They include important bench-mark and decision criteria that can be used to determine the successful development of an analytical technique or the success in meeting the stated goals and objectives of method development. After discussion with industry representatives, three end-state criteria were used for this evaluation: (1)

micronaire method agreement of ± 0.30 micronaire units for greater than 70% of the samples (reference HVI micronaire vs. portable NIR-determined micronaire); (2) rapid analyses (less than 5 min analysis time per sample); and (3) user-friendly/easy-to-use method that would require minimum operator training and technical expertise.

Chemometric Software and Data Analysis

All NIR calibrations and predictions were performed using the Camo® Unscrambler chemometric software package [22]. Derivative math and PLS calibrations were developed for the micronaire measurements. Calibration and method development was performed for two spectral regions – the entire spectrum (1100–2300 nm) and a tighter NIR spectral region with the peak at approximately 1930 nm removed from the calibration.

The entire spectrum from 1100–2300 nm has been shown to be an acceptable calibration spectral range for NIR micronaire calibrations with scanning instruments [14,15]. The large NIR absorbance at approximately 1930 nm observed for cotton fiber has been identified as due to fiber moisture [2]. In the laboratory analysis, cotton fibers can be maintained and conditioned at an equilibrium moisture content. However, not all cotton varieties have the same equilibrium moisture content at a specified laboratory temperature and RH, and not all laboratories use the same "standard" temperature and RH values and limits for their "controlled environment". These differences, though small, may impact the NIR results and end-state criteria results. Further, the NIR measurement of cotton fibers under tight environmental conditions is not possible for field measurements of micronaire, where moisture variation can occur due to large changes in environmental conditions (temperature, RH, overcast versus sunny, etc.). For these reasons, calibration and method development were also performed over a tighter NIR spectral region with the primary moisture peak at 1930 nm removed (1300–1800 nm/2000–2200 nm).

To determine the overall feasibility of the portable NIR analyzer to measure the cotton fiber micronaire in the laboratory and to meet end-state criteria, initial micronaire calibrations were developed with all 191 cotton samples. The primary comparison statistics to be used for the calibration samples were R^2, SEC (Standard Error of Calibration, a residual analysis for the calibration samples composed of the standard deviation of the differences between the HVI measured fiber micronaire and the portable NIR-determined fiber micronaire), and the percentage of samples in which the difference in the HVI and portable NIR predicted micronaire results are > ± 0.30 micronaire units (outliers > ± 0.30 micronaire units). The higher R^2, lower SEC, and lower the percentage of samples > ± 0.30 micronaire units, the better the portable NIR model for micronaire measurements.

Calibration results can demonstrate the feasibility of a NIR measurement, but the use of an external set of samples (not included in the calibration) is often utilized to validate and determine the robustness and full potential of a NIR measurement. The external validation set of samples is called the "Prediction Set." In addition to evaluating the calibration statistics on the 191 cotton samples, the 191 cotton samples were split into two sets – a 141-sample Calibration Set and a 50-sample Prediction Set. The 50 Prediction Set samples were selected so that each of the three sample groups was well represented and so that a wide, well-dispersed micronaire range was present within the Prediction Set. The primary comparison statistics to be used for the validation samples were R^2, SDD (Standard Deviation of Differences, a residual analysis for the prediction samples composed of the standard deviation of the differences between the HVI measured fiber micronaire and the portable NIR-determined fiber micronaire), and the percentage of samples in which the difference in the HVI and portable NIR predicted micronaire results are > ± 0.30 micronaire units (outliers > ± 0.30 micronaire units). The higher R^2, lower SDD, and lower the percentage of samples > ± 0.30 micronaire units, the better the portable NIR statistical model for measuring micronaire and meeting end-state criteria.

Results and Discussion

A program was implemented at the Southern Regional Research Center to determine the ability of portable NIR instrumentation and techniques to monitor critical cotton fiber properties of cotton samples in the laboratory, at-line, and in the field, with initial emphasis on cotton fiber micronaire analyses in the laboratory. This program consisted of qualitative NIR spectral analyses and quantitative NIR laboratory comparative evaluations in order to obtain the optimal instrument/operational conditions and settings for laboratory analyses. In addition to establishing a rapid and precise laboratory measurement of cotton fiber micronaire with portable NIR instrumentation, this program and operational optimization would provide valuable insight into the potential for at-line and field (non-laboratory) NIR measurements of fiber micronaire.

Qualitative NIR Spectral Analyses

Qualitative spectral analyses were performed on several of the wide micronaire range cotton fiber samples on the portable NIR analyzer. A typical cotton fiber NIR absorbance spectrum for the portable NIR analyzer and for a typical bench-top NIR analyzer (FOSS XDS, FOSS NIRSystems, Silver Spring, MD) is given in Figure 2. Very good NIR spectral and between-instrument agreement for both the porta-
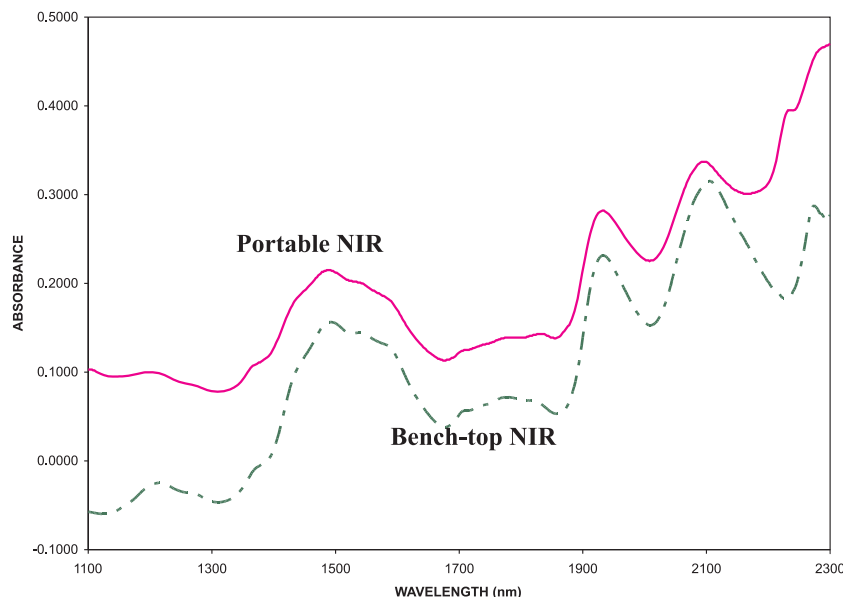
Figure 2 Comparison of typical NIR absorbance spectrum, cotton fiber, portable NIR analyzer and bench-top NIR analyzer (Foss XDS), 1100–2300 nm.
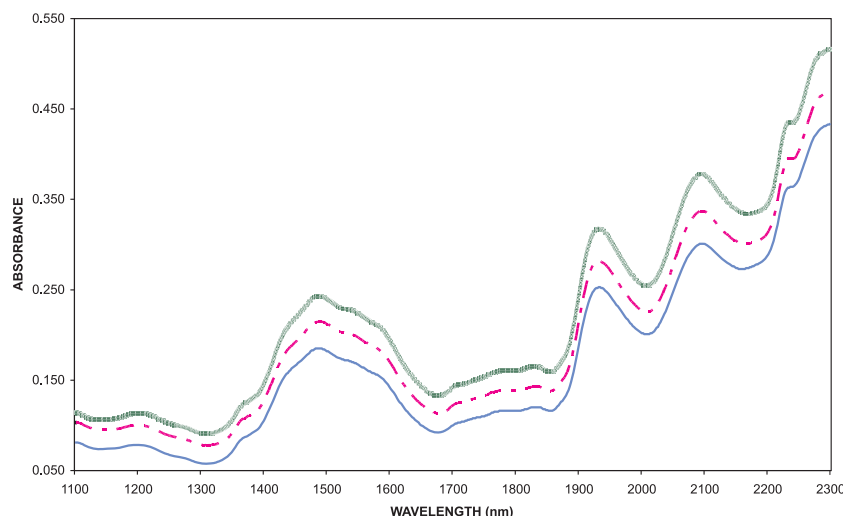

Figure 3 NIR absorbance spectra for cotton fiber samples with different micronaire values (Blue line = 2.90, Purple dotted = 4.10, Green pattern = 5.44 micronaire units).

ble and bench-top instruments were observed up to ~2200 nm, with several major cotton absorption peaks and regions clearly identified in both spectra.

NIR spectral differences were observed with the portable NIR analyzer for the absorbance spectra between samples with varying micronaire (Figure 3). However, significant differences ("shift") were observed between the baselines of the spectra. This "shift" or movement of spectral baseline is often observed for fiber NIR absorbance spectra. The differences in peak intensities in going from low to high micronaire is due to an increase in wall thickness that results in increase in optical path length of the source radiation. As to the baseline shifts, one cause is the

change in fiber cross-sectional perimeter which causes changes in light scattering.

The baseline shift can be minimized by several techniques, to include the use of a baseline correction and the use of derivatives. As observed in Figures 4 and 5, the baseline shift from a portable NIR analyzer is significantly minimized for the baseline-corrected absorbance spectra and for the first derivative spectra. The distinct spectral differences with varying micronaire values are readily observed for both the baseline-corrected and first derivative spectra. For the baseline-corrected spectra, major spectral differences with increasing micronaire value were observed at ~1490, 1535, 1930, 2100, and 2235 nm. The peaks at 1490

Figure 4 NIR absorbance spectra, baseline corrected, for cotton fiber samples with different micronaire values (Blue line = 2.90, Purple dotted = 4.10, Green pattern = 5.44 micronaire units).
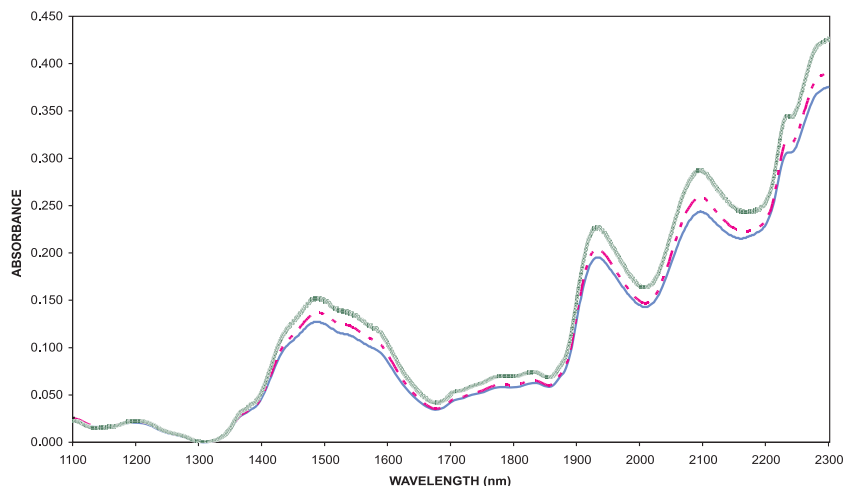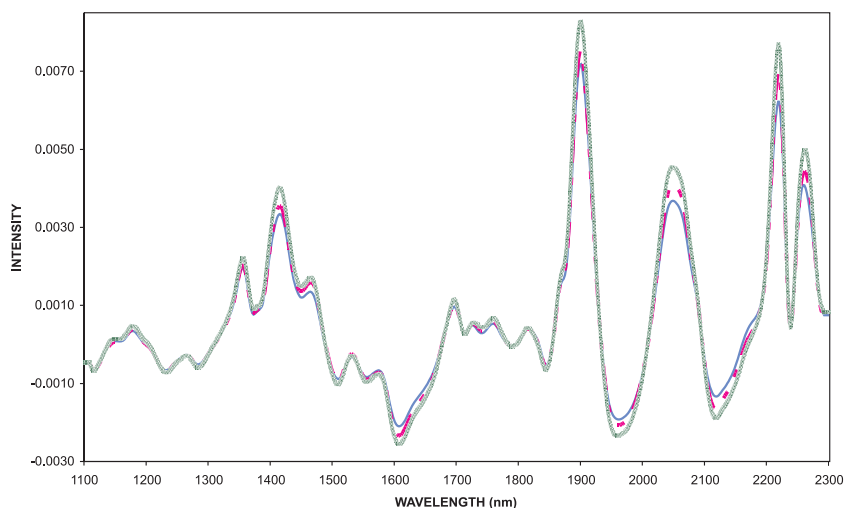

Figure 5 NIR first derivative spectra for cotton fiber samples with different micronaire values (Blue line = 2.90, Purple dotted = 4.10, Green pattern = 5.44 micronaire units).

and 1930 nm are often denoted as "moisture" peaks resulting from the OH first overtone from ~1400–1500 nm and the OH combination from ~1900–2000 nm. Pervious evaluations have shown that the 1930 nm peak is due primarily to OH absorbance for water/moisture [2]. However, the strong absorbances at 1490 nm and ~2100 nm were due to the OH groups present in cotton as well as moisture. Hence, the primary moisture band for cotton fiber is 1930 nm, while all other strong absorbing bands are strongly influenced by cotton species (OH overtone and combination and CH_n combination bands). The absorbances at 1490/1535 nm, 2100 nm, and 2235 nm are known cotton bands [2,10,17]. Since moisture differences may influence the NIR results, all cotton fiber samples were equilibrated in the laboratory for 24 h prior to NIR measurement.

For the first derivative spectra, several spectral regions with major spectral differences with increasing micronaire

value were observed, primarily at 1415, 1465, 1608, 1900 and 1960 nm (moisture bands), 2048, 2118, 2218 and 2260 nm. The large number of wavelengths/wavelength regions with readily apparent spectral differences with increasing micronaire value for the portable NIR analyzer indicated a distinct potential for rapid and precise micronaire measurements in the laboratory, leading to the quantitative evaluations.

Quantitative NIR Laboratory Analyses

A prime objective of the laboratory quantitative evaluations was the establishment of the optimal instrumental conditions and settings to employ with the NIR analyzer so as to meet and, if feasible, exceed the minimum requirements stated in the end-state criteria. After extensive discussions with the vendor and preliminary evaluations in the

Table 2 Settings/conditions for the instrumental and operational optimization.

VARIABLE	INSTRUMENT/OPERATIONAL CONDITION			
	NG1	G1	NG2	G2
Sampling Port	WITHOUT GLASS	WITH GLASS	WITHOUT GLASS	WITH GLASS
Instrument Gain	X1	X1	X2	X2

Table 3 First derivative PLS NIR calibration statistics, four measurement conditions (1300–1800 nm/2000–2200 nm), $n = 191$.

ITEM	MICRONAIRE (MIC)				
	HVI	NIR			
		NG1	G1	NG2	G2
AVG	4.22	4.22	4.22	4.22	4.22
R^2	NA	0.87	0.88	0.88	0.91
SEC	NA	0.21	0.20	0.20	0.17
No.>± 0.3 (%)	NA	15.7	19.8	14.7	10.8

NOTES:
1. NG1: Brimrose 5030 NIR, No Glass, Gain = 1
2. G1: Brimrose 5030 NIR, Glass, Gain = 1
3. NG2: Brimrose 5030 NIR, No Glass, Gain = 2
4. G2: Brimrose 5030 NIR, Glass, Gain = 2

laboratory, it was decided that the two instrumental settings and operational criteria that most impacted the NIR results for this portable NIR analyzer for fiber measurements were instrument gain and the type of "measuring head" or sampling port used. The portable NIR unit has two types of 5 mm sampling ports – open (no glass), and with a sapphire glass cover (with glass). Thus, a comparative evaluation was implemented to determine the optimal combination of instrument gain and sampling port type. Four combinations of settings/conditions were evaluated for all samples (Table 2):

1. Instrument Gain = 1, No Glass (open) Sample Port (condition NG1);
2. Instrument Gain = 1, Glass (Sapphire Glass) Sample Port (condition G1);
3. Instrument Gain = 2, No Glass (open) Sample Port (condition NG2);
4. Instrument Gain = 2, Glass (Sapphire Glass) Sample Port (condition G2).

A sample set of 191 cottons, with a wide range of micronaire and of different varieties, was measured for each condition, and their results compared.

Calibration Models, Full Sample Set

Initial micronaire calibration development was initiated with the 191 cotton samples measured with the four above

conditions. PCA often indicated three distinct sample groupings that were representative of the three groups/sample sets used to prepare the micronaire calibration database (Table 1). PLS calibrations and method development were completed for the four conditions with the base 191 samples. Often, derivative math is used for solid samples that exhibit a moderate or higher potential for baseline movement or scatter with repeat measurements (e.g., fibers). In addition, derivative math can be used to accentuate small spectral differences between samples that could be critical to robust NIR chemometric calibrations. Two forms of derivative math were used and combined with PLS for these investigations – the vendor-recommended first derivative and second derivative. Based on spectral analyses, the spectral ranges used for calibration development were 1100–2300 nm (full range, to include moisture peaks) and 1300–1800 nm/2000–2200 nm combination (removal of noisy derivative areas and the 1930 nm primary moisture peak; Figure 6). For all conditions, very good first derivative calibration statistics were obtained, with $R^2 > 0.80$, low residuals (SEC < 0.25 micronaire units), and over 75% of the samples agreed within ± 0.30 micronaire units (Table 3 and Figure 7). For each condition, improvements in calibration statistics were normally observed when the primary moisture peak at 1930 nm was removed from the calibration (1300–1800 nm/2000–2200 nm spectral regions). The best preliminary calibration results were observed with the "with glass, gain = 2" G2 method,

Figure 6 Moisture peak at approximately 1930 nm in a typical NIR absorption spectra for cotton, 1100–2300 nm.
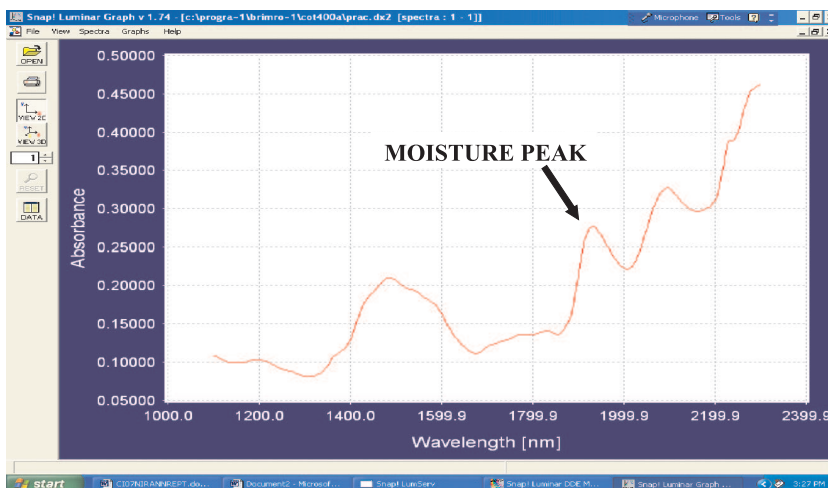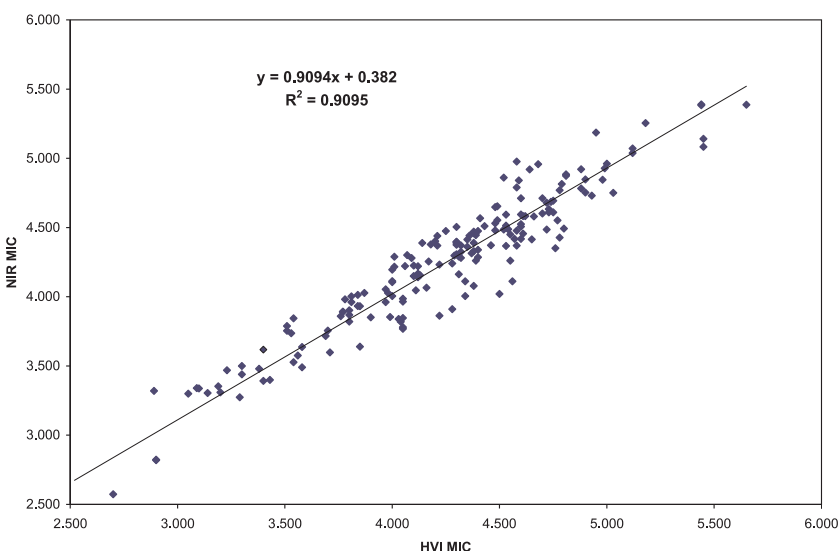

Figure 7 Micronaire comparison, G2 condition, first derivative PLS, 191 cotton samples.

in which over 89% of the samples agreed within ± 0.30 micronaire units. These calibration results demonstrate that the NIR measurement of cotton micronaire, using a portable NIR analyzer, is feasible.

Validation Protocol

Whereas calibration results can demonstrate the feasibility of an analysis, the robustness and full potential of an analysis requires the validation of the calibration on an external set of samples that have not been used in the calibration itself (a "Prediction Set"). To determine the robustness and full potential of the NIR measurement of cotton micronaire with the portable NIR unit, the base 191 samples were split into two sub-sets – a 141-sample calibration set and a 50-sample prediction set. It is not unusual for the validation statistics to be somewhat less than observed for

the calibration statistics, due to fewer samples being used in the new calibrations (141 samples instead of 191 samples) and now the prediction samples are not part of the calibration (not "fitted" for the calibration). For each of the four measurement conditions, new first derivative NIR calibrations were developed with the 141 sample calibration set, with the same spectral regions/combinations used for the 191 sample calibrations. The calibrations were then validated with the 50-sample prediction set (same samples for all four conditions). Next, the same validation protocol was used with second derivative NIR calibrations.

First Derivative Models with Validation

For all conditions, very good validation statistics were obtained with the first derivative calibrations, with $R^2 >$ 0.70, low residuals (SDD ≤ 0.30 micronaire units), and over

Table 4 First derivative PLS NIR validation statistics, four measurement conditions (1300–1800 nm/2000–2200 nm), $n = 50$.

ITEM	PREDICTION, MICRONAIRE (MIC)				
	HVI	NIR			
		NG1	G1	NG2	G2
AVG	4.20	4.21	4.17	4.22	4.22
R^2	NA	0.81	0.79	0.74	0.87
SDD	NA	0.26	0.27	0.30	0.22
No. > ± 0.3 (%)	NA	18.0	24.0	20.0	10.0

NOTES:
1. NG1: Brimrose 5030 NIR, No Glass, Gain = 1
2. G1: Brimrose 5030 NIR, Glass, Gain = 1
3. NG2: Brimrose 5030 NIR, No Glass, Gain = 2
4. G2: Brimrose 5030 NIR, Glass, Gain = 2

75% of the samples agreed within ± 0.30 micronaire units (Table 4 and Figure 8). Once again, improvements in calibration statistics were normally observed for each condition when the primary moisture peak at 1930 nm was removed from the calibration (1300–1800 nm/2000–2200 nm spectral region). The best validation results were observed with the "with glass, gain = 2" G2 method, in which 90% of the samples agreed within ± 0.30 micronaire units. Analysis time was less than 3 min per sample, and the portable NIR analyzer was very easy to use. Although the NIR micronaire analysis is not as fast as the reference HVI micronaire analysis, its NIR analysis time is rapid and very acceptable when one considers that the NIR analyzer is more cost effective (~10% of the cost of a HVI unit), portable (easily moved from one laboratory to another), does not require highly trained operators, does not require special utilities (e.g., high-pressure air), and has potential for multiple simultaneous analyses and non-laboratory measurements. In addition, the NIR analysis time was well below the end-state criteria for a "rapid analysis" estab-

lished by cotton industry representatives. Thus, all end-state criteria were successfully met. These validation results demonstrate and validate that the NIR measurement of cotton micronaire, using the portable NIR analyzer, is feasible and is capable of moderate-to-high agreement with the HVI micronaire values. For laboratory measurements, the G2 condition was shown once again to be the superior instrument setting for cotton fiber micronaire, in which all end-state conditions were either met or exceeded.

Second Derivative Models with Validation

Second derivative chemometric models were developed, and their prediction results compared with the micronaire prediction results from the first derivative chemometric models. Second derivative PLS chemometric calibrations, both with and without the 1930 nm moisture peak region, were developed. The calibration statistics for all 191 samples were very good for each condition, with low residuals (SDD), high R^2 values, and over 75% of the samples agree-
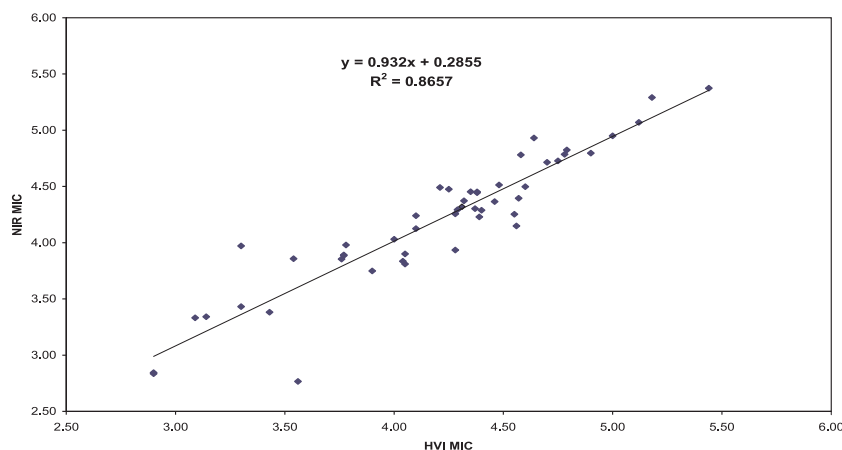

Figure 8 Validation results for micronaire, G2 condition, first derivative PLS, 50 cotton samples, 1300–1800 nm/2000–2200 nm spectral region.

Table 5 Second derivative PLS NIR validation statistics, four measurement conditions (1300–1800 nm/2000–2200 nm), $n = 50$.

| ITEM	HVI	PREDICTION, MICRONAIRE (MIC)			
		NIR			
		NG1	G1	NG2	G2
AVG	4.20	4.20	4.16	4.13	4.20
R^2	NA	0.75	0.78	0.82	0.87
SDD	NA	0.29	0.28	0.25	0.21
No. > ± 0.3 (%)	NA	30.0	20.0	24.0	12.0

NOTES:
1. NG1: Brimrose 5030 NIR, No Glass, Gain = 1
2. G1: Brimrose 5030 NIR, Glass, Gain = 1
3. NG2: Brimrose 5030 NIR, No Glass, Gain = 2
4. G2: Brimrose 5030 NIR, Glass, Gain = 2

ing within ± 0.30 micronaire units (HVI versus NIR). As mentioned previously, the robustness and full potential of an analysis requires the validation of the calibration on an external set of samples that have not been used in the calibration itself (a "Prediction Set"). Second derivative PLS calibrations were developed for the 141-sample Calibration Set for each condition, and these calibrations were validated on the 50-sample Prediction Set. Very good calibration statistics were observed, with low residuals/SDD, high R^2 values, and over 70% of the samples agreeing within ± 0.30 micronaire units (HVI versus NIR). Very good prediction results were also observed, with low residuals, high R^2 values, and at least 70% of the samples agreeing within ± 0.30 micronaire units (Table 5 and Figure 9). The differences in validation results were very small between the "with moisture" calibrations (full spectral region, 1100–2300 nm) and the "without moisture" calibrations in which the primary moisture peak at 1930 nm was

removed from the calibration (1300–1800 nm/2000–2200 nm spectral region).

Comparability, First and Second Derivative Model Validation

Since environmental conditions may influence the NIR results, the second derivative NIR results for the 1300–1800 nm/2000–2200 nm spectral region were used for this evaluation and comparison with the first derivative PLS calibrations. The best validation results were observed once again with the "with glass, gain = 2" G2 method, in which 88% of the samples agreed within ± 0.30 micronaire units. However, the observed advantage of "with glass"/G conditions over "without glass"/NG conditions were more readily apparent for the second derivative PLS calibrations, with fewer outliers, slightly lower SDDs, and slightly higher R^2s for each G condition compared with the corre-
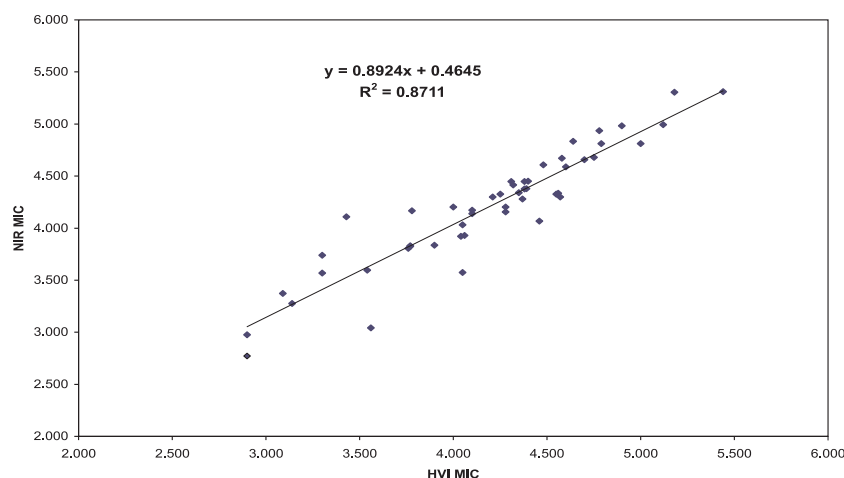
Figure 9 Validation results for micronaire, G2 condition, second derivative PLS, 50 cotton samples, 1300–1800 nm/2000–2200 nm spectral region.

y = 0.8924x + 0.4645
R^2 = 0.8711

sponding NG condition. Analysis time was less than 3 min per sample, and the portable NIR analyzer was very easy to use. Thus, all end-state criteria were successfully met.

Therefore, the rapid, precise, and accurate laboratory measurement of cotton fiber micronaire with portable NIR instrumentation was demonstrated. These validation results demonstrate and validate that the NIR laboratory measurement of cotton micronaire, using a portable NIR analyzer, is feasible and is capable of moderate-to-high agreement with the HVI micronaire values. Overall, the second derivative PLS calibration and prediction results were in good agreement with the calibration and prediction results obtained with first derivative PLS calibrations, but they did not exhibit a significant improvement over the first derivative PLS NIR results on laboratory samples. Since only small differences were observed between the first derivative PLS and the second derivative PLS prediction results, either method may be used. Both calibration systems clearly demonstrated that the "with glass"/G2 condition is the best overall condition for the laboratory measurement of cotton fiber micronaire by a portable NIR analyzer. Future work will investigate at-line and field measurements of cotton fiber micronaire by portable NIR analyzer, utilizing the "with glass"/G2 measurement method.

Conclusions

A program was implemented to determine the feasibility and capabilities of portable NIR instrumentation to perform rapid and accurate laboratory measurements of cotton fiber micronaire. Micronaire is a key cotton fiber property, and it is an indicator of the fiber's maturity and fineness. Spectral evaluations demonstrated very good NIR spectral agreement between portable and bench-top NIR units for micronaire, with all major absorbencies for cotton fiber observed with the portable NIR analyzer. Distinct NIR spectral differences between samples with varying micronaire were readily observed for baseline-corrected NIR absorbance spectra and first derivative NIR spectra. The basic optimal instrumental and operational conditions and settings for cotton fiber laboratory micronaire measurements by the portable NIR analyzer were established, with the best overall laboratory micronaire results obtained with the use of a glass-covered sampling port ("with glass") and increased instrumental gain. The NIR measurement was fast (< 3 min per sample) and easy to perform. All end-state criteria were met. Both first derivative and second derivative PLS calibrations clearly demonstrated that the "with glass"/gain = 2 (G2) condition was the best overall condition for the laboratory measurement of cotton fiber micronaire by a portable NIR analyzer. For both first and second derivative PLS calibrations, very good validation results were obtained with the optimal condition, with high R^2, low residuals, and with less than 12% outliers. The

rapid, precise, and accurate laboratory measurement of cotton fiber micronaire with portable NIR instrumentation was demonstrated.

Disclaimer

The use of a company or product name is solely for the purpose of providing specific information and does not imply approval or recommendation by the United States Department of Agriculture to the exclusion of others.

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